Characterization of fluoroelastomers by various analytical techniques including pyrolysis gas chromatography/mass spectrometry☆

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ABSTRACT

Fluorocarbon elastomers are specified for a number of applications where excellent high temperature and chemical resistance is required. To ensure that a fluoroelastomer with the required properties for a particular application is used, characterization techniques that allow the positive identification of the elastomer are required. In this paper the characterization of four fluoroelastomer formulations – a vinylidene fluoride/hexafluoropropene (VDF/HFP) dipolymer, a vinylidene fluoride/hexafluoropropene/tetrafluoroethylene terpolymer, and two vinylidene fluoride/perfluoro(methyl vinyl ether)/tetrafluoroethylene (VDF/PMVE/TFE) tetrapolymers – is described. The characterization techniques included pyrolysis gas chromatography/mass spectrometry (py-GC/MS), Fourier transform infrared (FT-IR) spectrometry, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Py-GC/MS was the only characterization technique that could identify the four formulations unambiguously. The positive identification was based on differences in the pyrolytic degradation products of the flouroelastomer formulations.

1. Introduction

Fluoroelastomers have excellent chemical and heat resistance and because of this are specified for applications where these properties are required. They are used in the marine, automotive, aerospace, oil, and chemical industries as seals, O-rings, gaskets, and fuel hoses. The properties of a particular fluorocarbon elastomer composition depend on several factors. These include the monomers and curing agent used in their preparation. The fluid resistance of fluoroelastomers generally improves as the fluorine content of the elastomer increases. Peroxide cured fluoroelastomers have superior water and acid resistance compared to those cured with bisphenol based compounds while the bisphenol cured fluoroelastomers have superior thermal stability compared to those cured with peroxides [1].

There are several monomers used to prepare commercial fluoroelastomers. These include 1,1-difluoroethylene or vinylidene fluoride (VDF), tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and perfluoro(methyl vinyl ether) (PMVE). Although fluoroelastomers have excellent fluid and heat resistance, some of the formulations have glass transition temperatures (T_g) that make

them unsuitable for applications where lower temperatures may be encountered. For instance, VDF/HFP/TFE fluoroelastomers have a T_g of approximately $-13\,^\circ$C while VDF/HFP fluoroelastomers have a T_g of approximately $-20\,^\circ$C. To overcome this limitation, fluoroelastomers containing PMVE have been developed. These VDF/PMVE/TFE fluoroelastomers can have a T_g as low as approximately $-30\,^\circ$C depending on the weight percent fluorine in the elastomer [1].

Because of the relationship between the formulation, properties and performance of these elastomers, it is important to ensure that a fluoroelastomer with the required formulation is used in a particular application. When a particular elastomer fails in-service or has to be replaced, it is also important to make certain that the correct elastomer was used and that the correct elastomer is used to replace the failed elastomer. To enable this, analytical techniques that can positively identify fluoroelastomer types are required.

Pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) has been used to identify a broad range of polymeric materials including thermoplastics, thermoset resins, elastomers and paints [2–10]. Concerning fluoropolymers, Lonfei et al. [11] studied the pyrolytic degradation mechanisms of a number of thermoplastic fluoropolymers using pyrolysis packed column GC/MS and pyrolysis MS. Several of the fluoropolymers were synthesized from the same monomers as those used in the fluoroelastomers studied in this paper. They found for perfluoropolymers, such as a TFE/HFP copolymer, that depolymerization predominates during pyrolysis. The degradation involves random scission of the carbon chains followed by alpha cleavage of neighboring carbon–carbon bonds

to release the monomers. However, they also observed that the introduction of PMVE or VDF into the polymers results in a significant change in the degradation mechanisms. The presence of perfluoromethoxy groups activate the fluorine atom attached to the same carbon. This results in random chain scission accompanied by fluorine transfer and leads to the formation of large amounts of perfluoroalkanes and perfluoroalkenes. When monomers containing hygrogen atoms, such as VDF, are present in the polymer, the degradation mechanisms include the elimination of hydrogen fluoride accompanied by hydrogen transfer. Hydrogen transfer accompanied by random chain scission leads to the formation of alkanes and terminal alkenes.

In this paper the identification of four fluoroelastomers using py-GC/MS is described. The identification is based on differences in the major pyrolytic degradation products produced by each of the fluoroelastomers. These differences are discussed with respect to the degradation mechanisms reported in reference [11]. The results of other techniques including Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are presented and their usefulness in the characterization and identification of fluoroelastomers is discussed.

2. Experimental

2.1. Materials

The four fluoroelastomers used in this study were purchased from James Walker MFG. Co., Glenwood, Illinois. They were designated as FR10/80, FR17/75, FR25/80, and LR6316/75. These compounds are similar to fluoroelastomers that may be better known as 'viton' A (FR10/80), 'viton' B (FR17/75), GFLT (LR6316/75), and GLT (FR25/80).

FR10/80 fluoroelastomer is a copolymer of HFP and VDF. It is a general purpose fluoroelastomer with a low compression set and can be used in a temperature range between −18 °C and 200 °C. It has a Shore Durometer type A hardness of 80.

FR17/75 fluoroelastomer is a terpolymer of HFP, VDF and TFE. It is a general purpose fluoroelastomer with improved fuel resistance compared to FR10 fluoroelastomers and can be used in a
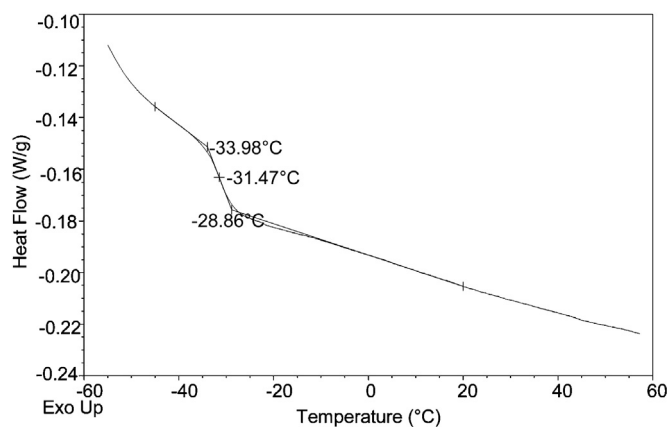

Fig. 1. Thermogram of FR 25/80 fluoroelastomer.

temperature range between −12 °C and 210 °C. It has a Shore Durometer type A hardness of 75.

LR6316/75 fluoroelastomer is a tetrapolymer containing VDF, TFE, and PMVE and is formulated to have improved low temperature properties compared to the FR10 and FR17 type fluoroelastomers and superior chemical resistance compared to FR25. It is a low temperature (LT) grade fluoroelastomer with high fluorine content and can be used in a temperature range between −29 °C and 205 °C. It has a Shore Durometer type A hardness of 75.

FR25/80 fluoroelastomer is a tetrapolymer containing VDF, TFE, and PMVE. It is a low temperature (LT) grade fluoroelastomer with superior rapid gas decompression properties. It can be used in a temperature range between −41 °C and 200 °C. It has a Shore Durometer type A hardness of 80.

2.2. Analysis

2.2.1. Pyrolysis gas chromatography/mass spectroscopy/mass spectroscopy

All pyrolysis were carried out in a platinum coil pyroprobe (Pyroprobe 5000, CDS, Oxford, PA). Approximately 0.1 mg of the sample was centered in a 25 mm quartz tube and heated to a final temperature of 700 °C, 800 °C or 900 °C using a heating ramp
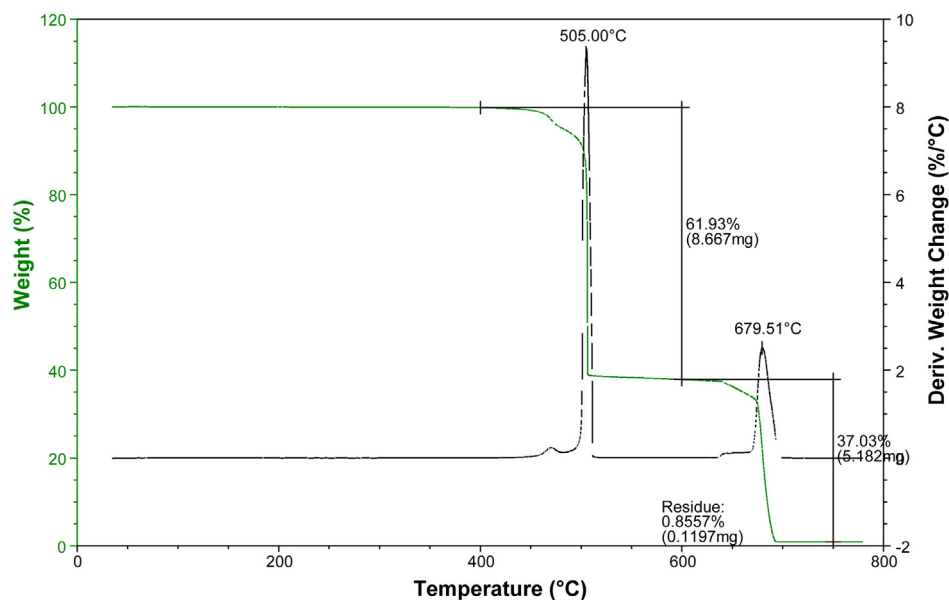

Fig. 2. Plots of % weight loss against temperature and the derivative of % weight change against temperature for the LR6163/75 fluoroelastomer.

Table 1
Average glass transition temperatures (T_g) of the four fluoroelastomers as measured by DSC.

Sample name	First weight loss (%)	T_{max1} (°C) of first weight loss	Second weight loss (%)	T_{max2} (°C) of second weight losss	Residue (%)
FR10/80	61.5 ± 0.4	487.9 ± 3.0	29.8 ± 0.5	661.8 ± 4.5	8.3 ± 0.2
FR17/75	70.0 ± 0.7	501.1 ± 1.0	18.8 ± 0.6	661.4 ± 4.4	10.5 ± 0.1
LR6316/75	62.1 ± 0.2	504.7 ± 0.6	36.8 ± 0.6	672.9 ± 5.8	0.8 ± 0.2
FR25/80	60.0 ± 0.1	497.1 ± 0.0	39.4 ± 0.1	677.5 ± 3.4	0.4 ± 0.1

of $20\,°C\,ms^{-1}$. The hold time at the final temperature was 20 s. The pyrolysis products were separated on a 30 m long × 0.25 mm inside diameter 5% phenyl polydimethylsiloxane capillary column (DB-5, J&W Scientific, Folsom, CA). The inlet was set to a split flow of $50\,mL\,min^{-1}$, with a split ratio of 50:1. The flow rate of the carrier gas (He) was $1\,mL\,min^{-1}$. The heating program used for the gas chromatograph (Trace GC Ultra, Thermo Scientific) consisted of holding the oven temperature at 40 °C for 4 min, then ramping the temperature to 300 °C at a rate of $10\,°C\,min^{-1}$, and finally holding the temperature at 300 °C for 10 min. Each GC run took 40 min to complete.

A Triple Stage Quadrupole (TSQ) (Thermo Scientific) MS/MS was used to detect the ions of the pyrolysis products. The MS/MS was used in the full scan mode. Each scan, from 50 atomic mass units (amu) to 500 amu, took 0.5 s.

2.2.2. Infrared analysis

All infrared spectra were acquired on a Vertex 70 Fourier Transform infrared spectrometer (Bruker Optics) using a single bounce attenuated total reflectance (ATR) accessory (Spectra-Tech Thunderdome, Thermo Scientific). The ATR was fitted with a germanium crystal. A background was obtained prior to acquiring the spectra of each fluoroelastomer. The spectra, acquired between $4000\,cm^{-1}$ and $600\,cm^{-1}$, were the average of 100 scans at a resolution of $4\,cm^{-1}$. All spectra were baseline corrected and normalized.

2.2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a Q500 thermogravimetric analyser (TA Instruments, New Castle, Delaware) using aluminum sample pans. Nitrogen (N_2) was used as the balance and sample gas at flow rates of $40\,mL\,min^{-1}$ and
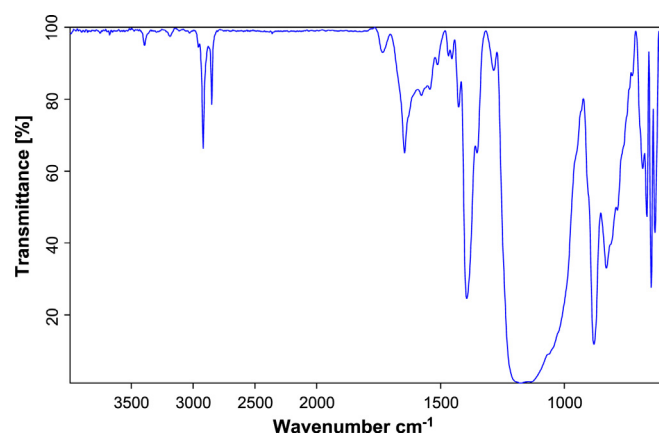
Fig. 3. FT-IR spectra of the FR10/80 fluoroelastomer.

$60\,mL\,min^{-1}$ respectively. The sample sizes ranged from ∼5 mg to ∼40 mg.

All analyses were carried out in the high resolution mode. The sample was held at 35 °C, and then the temperature ramped at a rate of $50\,°C\,min^{-1}$ until the rate of weight loss exceeded an operator selected rate. The temperature of the sample was then kept constant until the rate of weight loss dropped below an operator selected rate. The temperature ramp $50\,°C\,min^{-1}$ was then resumed until the temperature reached 650 °C. At 650 °C, the gas was changed from N_2 to air and the temperature ramp of $50\,°C\,min^{-1}$ resumed until the rate of weight loss exceeded the operator determined rate. The temperature of the sample was then kept constant until the rate of weight loss dropped below an operator selected rate. The temperature ramp was then resumed. The
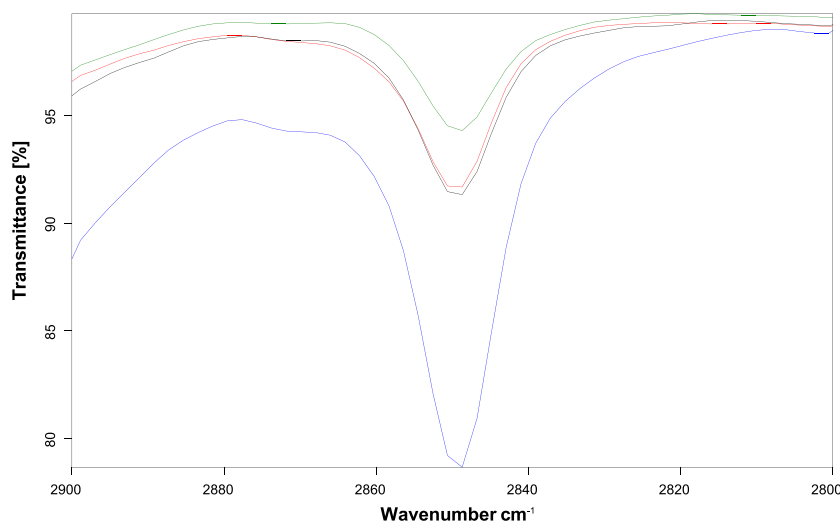
Fig. 4. Overlay of the FT-IR spectra of FR10/80 (blue), FR 17/75 (red), LR6316/75 (green), and FR25/80 (black) fluoroelastomers between $2900\,cm^{-1}$ and $2800\,cm^{-1}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
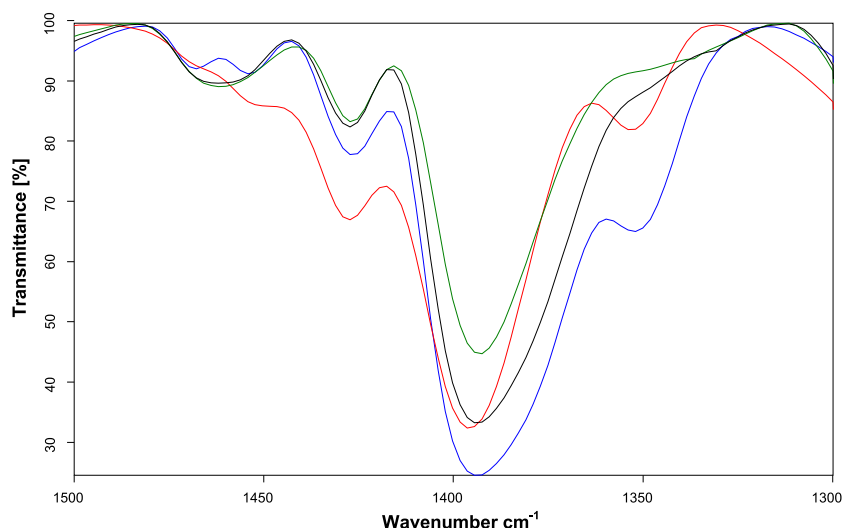
Fig. 5. Overlay of the FT-IR spectra of FR10/80 (blue), FR 17/75 (red), LR6316/75 (green), and FR25/80 (black) fluoroelastomers between 1500 cm^{-1} and 1300 cm^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
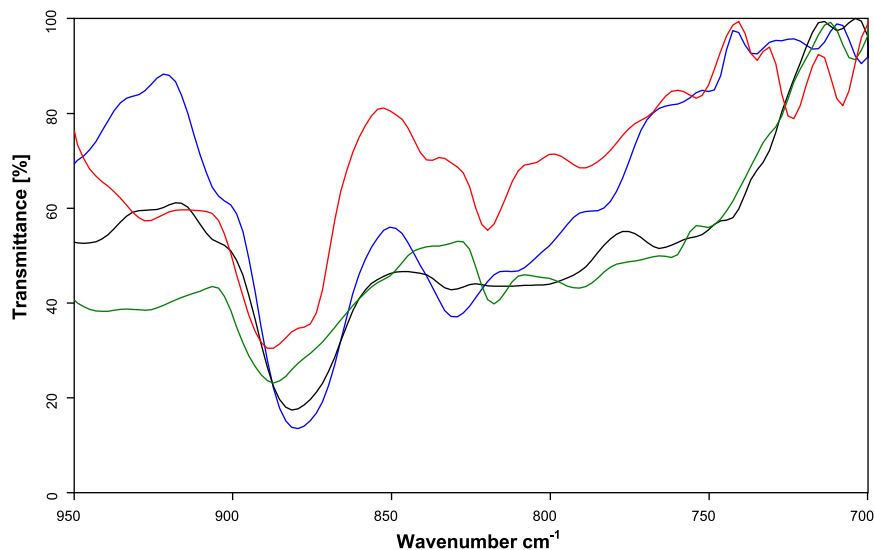

Fig. 6. Overlay of the FT-IR spectra of FR10/80 (blue), FR 17/75 (red), LR6316/75 (green), and FR25/80 (black) fluoroelastomers between 950 cm^{-1} and 700 cm^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

experiment was terminated at 800 °C. The reported percentage weight losses and temperatures of maximum rate of weight loss were the average values of three analyses.

2.2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out on a Q1000 differential scanning calorimeter (TA Instruments, New Castle, Delaware). The apparatus was calibrated using an Indium standard. The samples were held at −60 °C for a minute and then the temperature was ramped at a rate of 10 °C min^{-1} to 60 °C. The difference in heat flow (W g^{-1}) into the sample and the reference pans was recorded as a function of temperature. The T_g was calculated from the tangents to the heat flow versus temperature curve before the transition, after the transition and at the point in the transition with the maximum slope. The reported T_g was the average value of three analyses.

3. Results and discussion

3.1. Measurement of glass transition temperatures (T_gs) of the fluoroelastomers by DSC

The DSC thermogram of the FR25/80 fluoroelastomer is shown in Fig. 1. Thermograms are plots of heat flow versus temperature. At the T_g, the heat capacity of a material changes rapidly. This in turn affects the heat flow into the sample and therefore the slope of the heat flow versus temperature plot.

The T_g values for the four fluoroelastomers are listed in Table 1. The FR17/75 fluoroelastomer has the highest T_g (−12.7 °C), followed by FR10/80 (−16.8 °C), LR6316/75 (−25.0 °C), and FR25/80 (−31.3 °C) fluoroelastomers. The T_gs correspond well with published values [1] for 'viton' B, 'viton' A, GFLT and GLT fluoroelastomers.

DSC analyses provide good supporting evidence for the identification of polymeric materials. However, the T_g of a polymer is
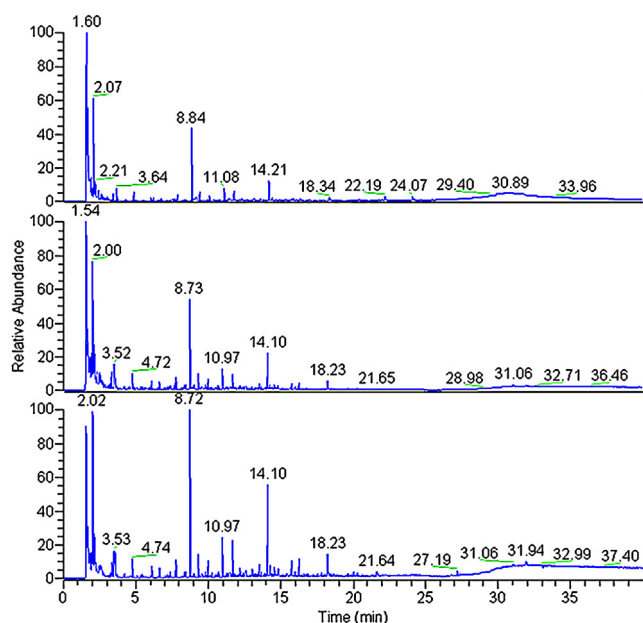
Fig. 7. Pyrograms of FR10/80 fluoroelastomer pyrolyzed at (top) 900 °C, (middle) 800 °C, and (bottom) 700 °C.

Fig. 8. Pyrograms of the FR10/80 fluoroelastomer pyrolyzed at (top) 900 °C, (middle) 800 °C, and (bottom) 700 °C between 3.5 and 15.0 min.

related to its composition, structure, for instance sequence distribution in copolymers and terpolymers, and the presence of additives [12]. The T_g of a polymer can be affected by a number of factors while in service, including the absorption of fluids and aging (thermal, oxidative, and ultra violet degradation). The absorption of fluids by a polymer most often leads to a reduction in the T_g of the sample through plasticization [13]. If a material has been in service and in contact with a fluid or fluids that act to plasticize the sample, the measured T_g will be lower than a sample of the same material that has not been exposed to the fluid. Thermal, oxidative or ultraviolet degradation can lead to a number of changes in the
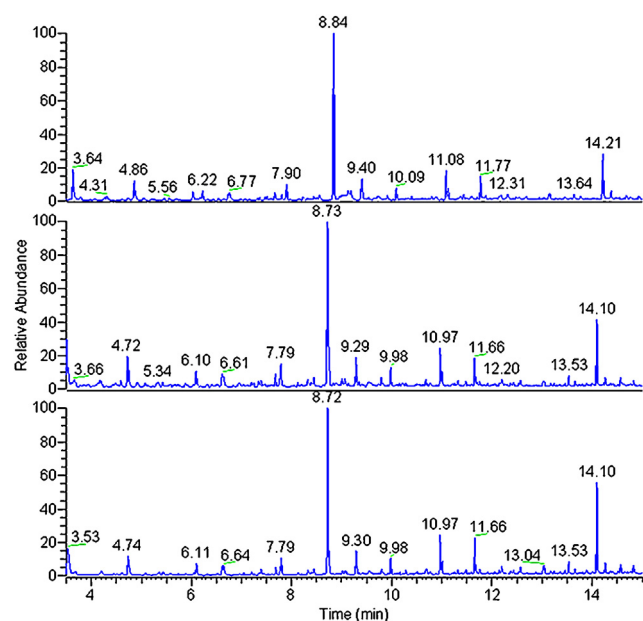
structure of a polymer. In some polymers degradation leads to an increase in cross linking in the polymer while in others it results in a decrease in cross linking. Additives, such as plasticizers, can also be lost from a polymer over time. The T_g of the polymer will reflect these changes.

3.2. Thermal stability of the fluoroelastomers by TGA

TGA plots of percent weight loss versus temperature and the derivative of percent weight loss versus temperature for the LR6316/75 fluoroelastomer are shown in Fig. 2. For each of the elastomers the weight loss in the TGA experiment was found to take
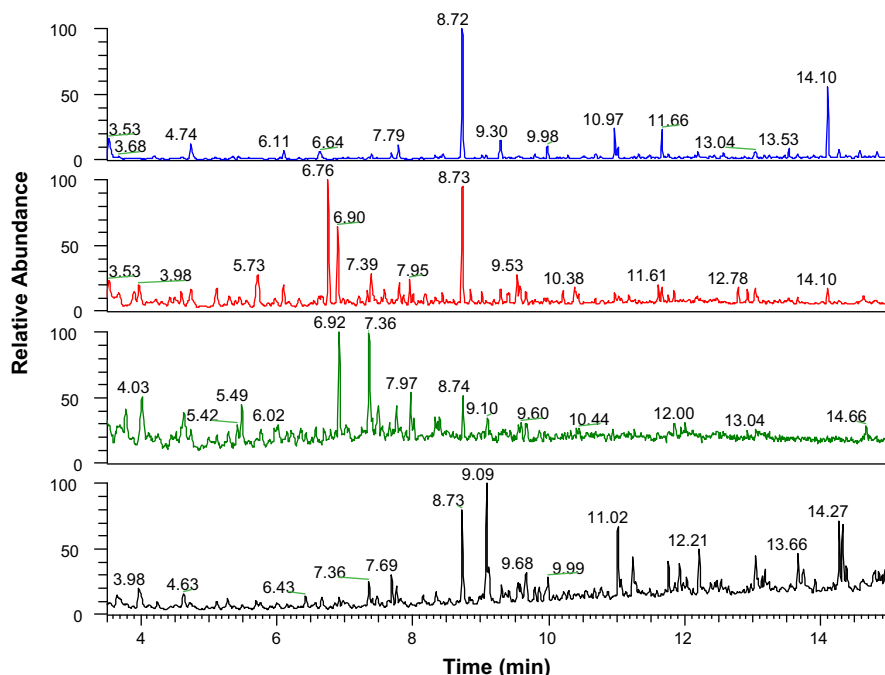

Fig. 9. Pyrograms, from top to bottom, of FR10/80, FR 17/75, LR6316/75, and FR25/80 fluoroelastomers between 3.5 and 15.0 min. All samples were pyrolyzed at 700 °C.
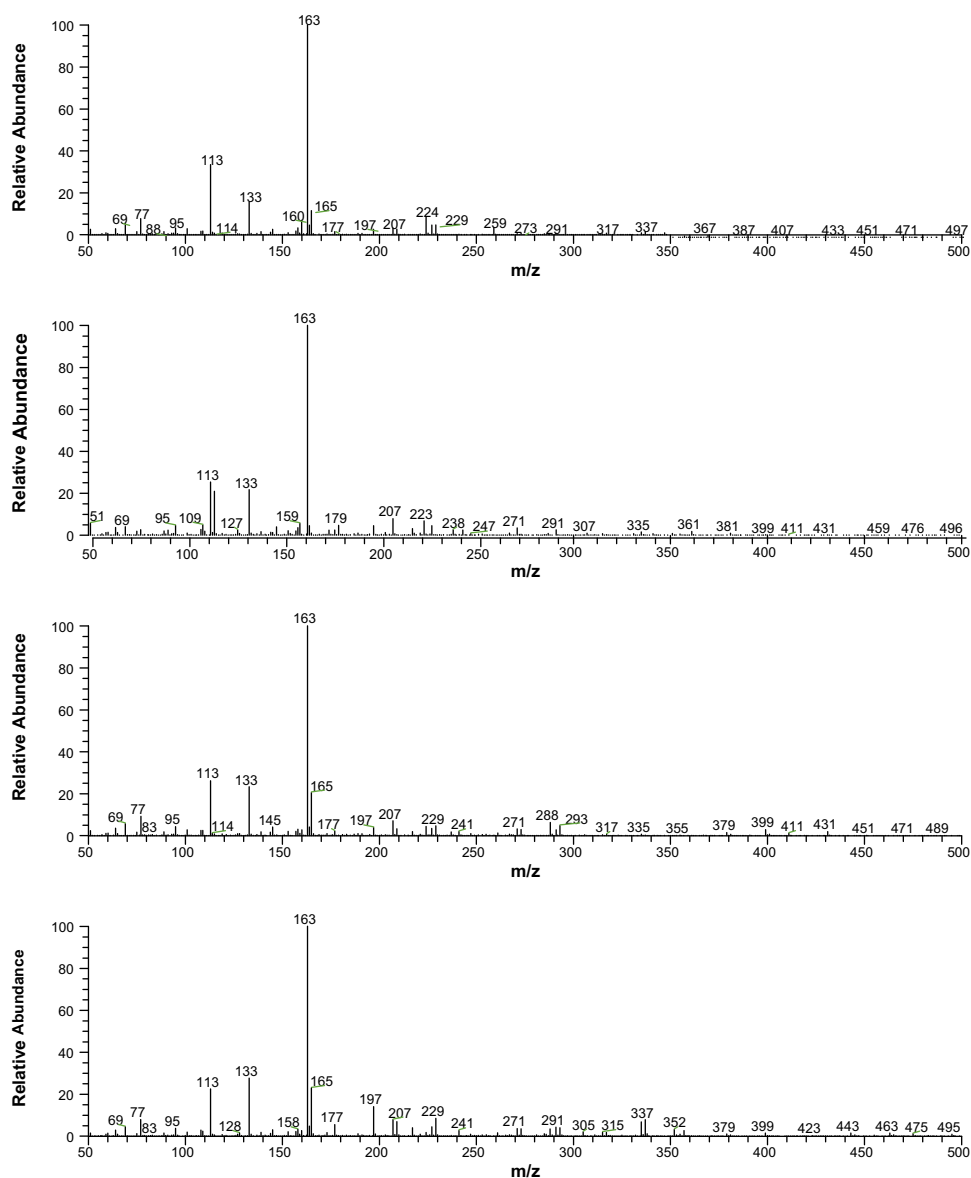
Fig. 10. Mass spectra of peaks (from top to bottom) at 8.73 min, 10.97 min, 11.66 min and 14.11 min in the pyrogram of the FR10/80 fluoroelastomer.

Table 2

First weight loss, second weight loss, temperatures of maximum rate of first and second weight losses and weight of residue of the four fluoroelastomers.

Sample name	Average T_g (°C)	Literature T_g (°C)
FR10/80	−16.8 ± 0.9	−18
FR17/75	−12.7 ± 0.2	−13
LR6316/75	−25.0 ± 0.2	−23
FR25/80	−31.3 ± 0.7	−29

place in two steps. The first was at approximately 500 °C and the second was at approximately 670 °C. The percent weight loss, the temperatures of the maximum rate of weight loss and the weight of residue for the four fluoroelastomers are listed in Table 2.

The percent weight loss in the first step was similar for FR10/80 (61.5 ± 0.4%), LR6316/75 (62.1 ± 0.2%), and FR25/80 (60.0 ± 0.1%) fluoroelastomers. However, the FR17/75 fluoroelastomer lost ∼70% (70.0 ± 0.7) of its weight in the first step. The temperature of maximum rate of weight loss, T_{max1}, for the first weight loss step was similar for FR17/75 (501.1 ± 1.0 °C), LR6316/75 (504.7 ± 0.6 °C), and

FR25/80 (497.1 ± 0.0 °C) fluoroelastomers while FR10/80 fluoroelastomer had a T_{max1} (487.9 ± 3.0 °C). This was approximately 10 °C lower than the other three fluoroelastomers.

The percent loss for the second weight loss step was different for each of the fluoroelastomers. The FR10/80 fluoroelastomer lost ∼30% (29.8 ± 0.5%), the FR17/75 fluoroelastomer lost ∼19% (18.9 ± 0.6%), the LR6316/75 fluoroelastomer lost ∼ 37% (36.8 ± 0.6%), and the FR25/80 fluoroelastomer lost ∼40% (39.4 ± 0.1). The temperature of maximum rate of weight loss for the second weight loss step, T_{max2}, was similar for the FR10/80 (661.8 ± 4.5 °C) and FR17/75 (661.4 ± 4.4 °C) fluoroelastomers. The T_{max2} for the LR6316/75 (672.9 ± 5.8 °C) and FR25/80 (677.5 ± 3.4 °C) fluoroelastomers were higher than the T_{max2} for the FR10/80 and FR17/75 fluoroelastomers.

The FR10/80 fluoroelastomer (8.3 ± 0.2%) and the FR17/75 fluoroelastomer (10.5 ± 0.1%) had significantly larger amounts of residue compared to the LR6316/75 (0.8 ± 0.2%) and the FR25/80 (0.4 ± 0.1%) fluoroelastomers. The larger percentage residues in the FR10/80 and FR17/75 fluoroelastomers are due to the presence of additives, such as fillers, in these elastomers.
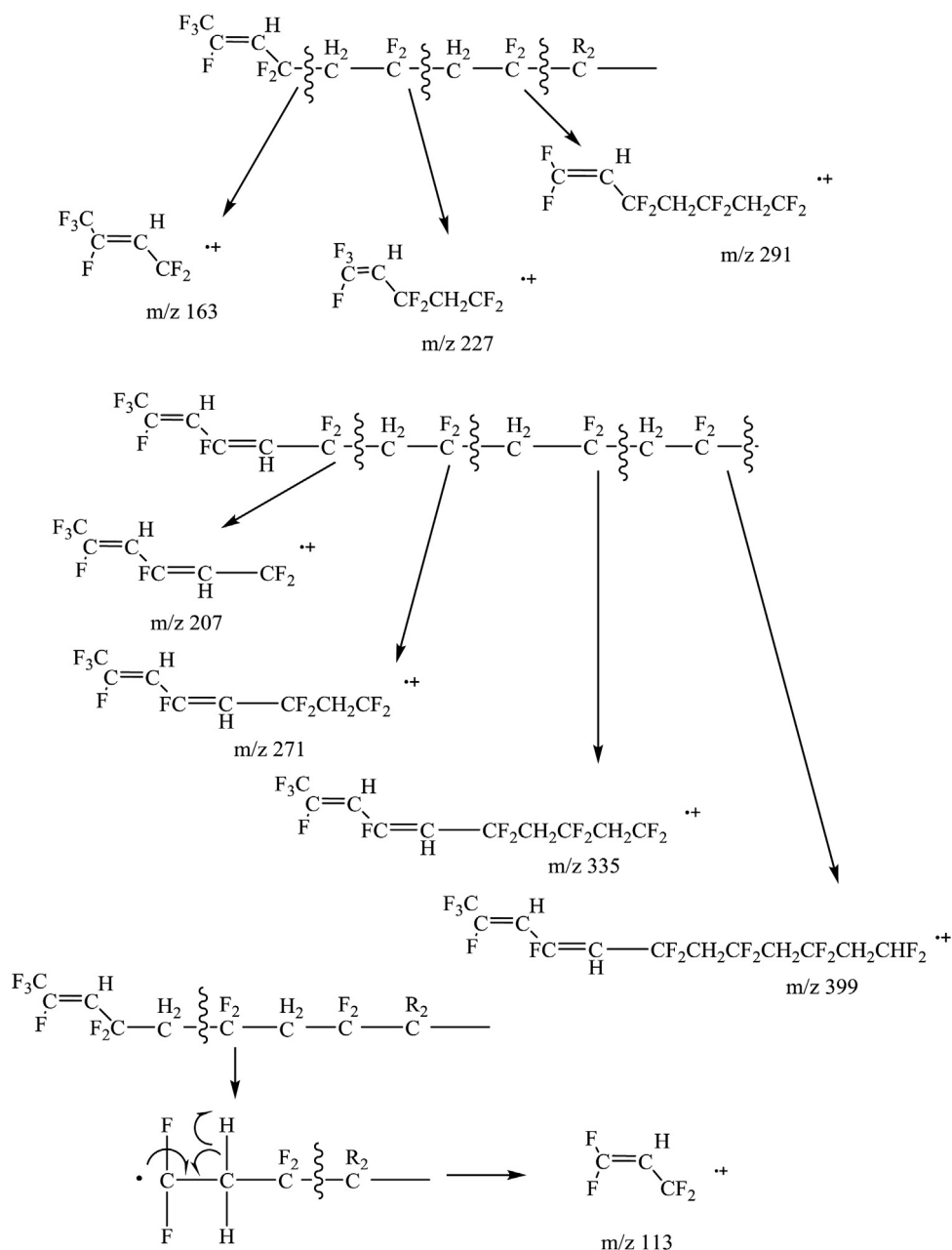
Fig. 11. Potential pathways for the formation of some of the ions in the mass spectra of the major degradation products of FR10/80.

The temperature at which a polymer degrades is directly related to its composition, that is, the monomeric material or materials used to synthesize it, and how these monomers react to form the polymer's structure. Therefore polymers with different compositions and structures will degrade at different temperatures. In general, TGA results provide good supporting information for the identification of polymeric materials. However, the technique by itself could only be used to identify a polymeric material if a known sample of the material was available to be used as a standard.

3.3. Characterization of the fluoroelastomers by Fourier transform infrared spectroscopy

The infrared spectrum of the FR10/80 fluoroelastomer is shown in Fig. 3. Although the IR spectra of the four fluoroelastomers were quite similar, there were differences in several regions of their IR spectra. Three areas will be discussed: from $2900 \, \text{cm}^{-1}$ to $2800 \, \text{cm}^{-1}$, from $1500 \, \text{cm}^{-1}$ to $1300 \, \text{cm}^{-1}$, and from $1000 \, \text{cm}^{-1}$ to $700 \, \text{cm}^{-1}$.

IR absorbance peaks between $2950 \, \text{cm}^{-1}$ and $2800 \, \text{cm}^{-1}$ are characteristic of symmetric and asymmetric C—H stretching. An expanded view of the IR spectra between $2900 \, \text{cm}^{-1}$ and $2800 \, \text{cm}^{-1}$ is shown in Fig. 4. As vinylidene fluoride is the only monomer used in these fluoroelastomers containing C—H bonds, the strength of the absorbance for a particular fluoroelastomer should correlate with the vinylidene fluoride content of that elastomer. Typical values [1] for the percentage of vinylidene fluoride in the four types of elastomers are 60% vinylidene fluoride for a copolymer fluoroelastomer such as the FR10/80, 54% vinylidene fluoride for a tetrapolymer fluoroelastomer such as FR25/80, 45% vinylidene fluoride for a terpolymer fluoroelastomer such as FR17/75, and 36% vinylidene fluoride for a tetrapolymer fluoroelastomer such a LR6361/75. Referring to Fig. 4, the FR10/80 fluoroelastomer has the most intense absorbance and LR6361/75 has the least intense
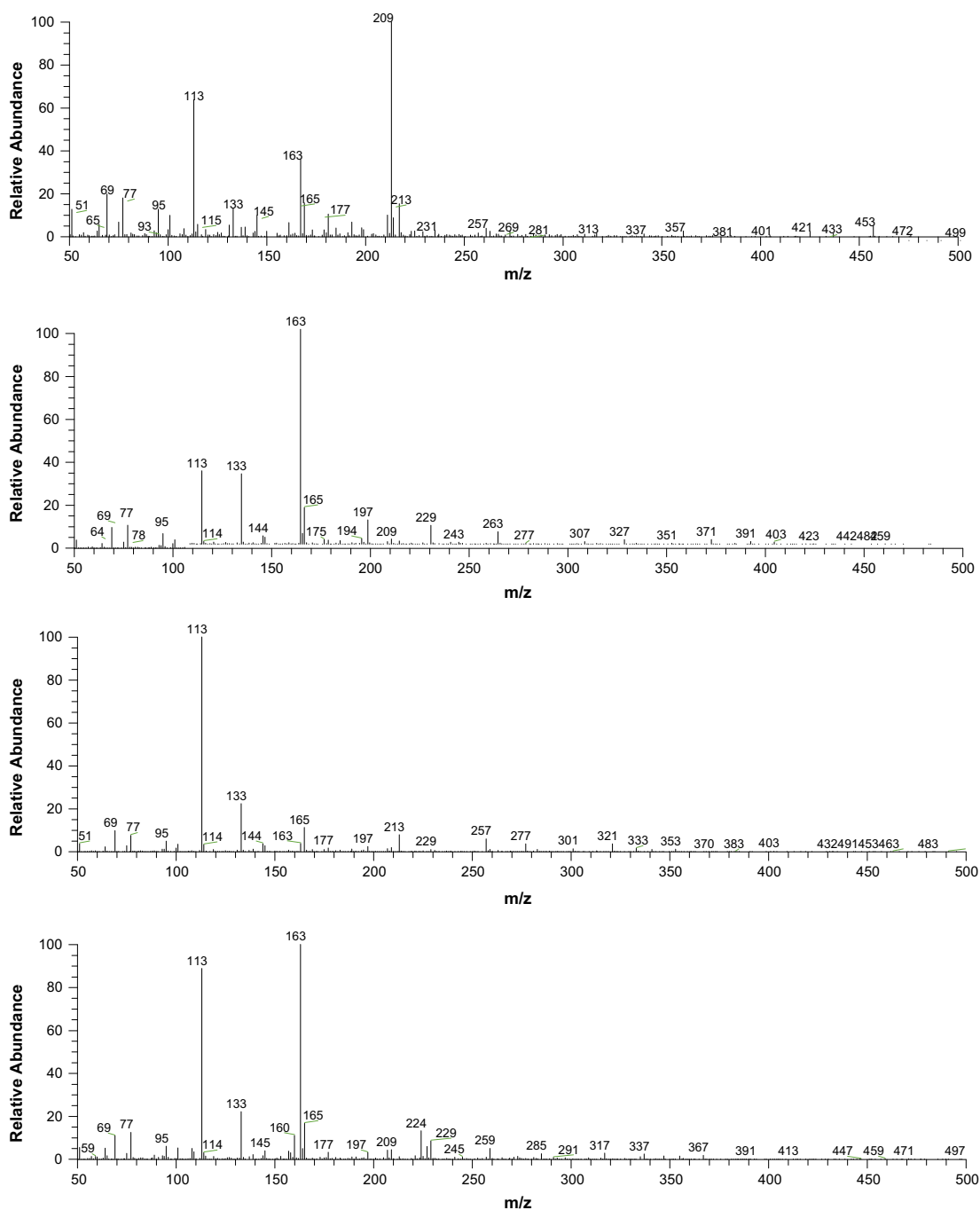
Fig. 12. Mass spectra, from top to bottom, of peaks at 5.72 min, 6.76 min, 6.90 min, and 8.73 min in the pyrogram of the FR17/75 fluoroelastomer.

absorbance. This corresponds well with the percentage of vinylidene fluoride in the elastomers.

Expanded views of the IR spectra between 1500 cm^{-1}, 1300 cm^{-1}, 950 cm^{-1} and 700 cm^{-1} are shown in Figs. 5 and 6 respectively.

There is a shoulder on the absorbance peak at 1350 cm^{-1} in the spectra of the FR10/80 and FR17/75 fluoroelastomers that is not present in the spectra of the LR6316/75 and FR25/80 fluoroelastomers. Comparison of the FR10/80 and FR17/75 fluoroelastomer spectra indicates that the FR17/75 fluoroelastomer has a weak absorbance peak at ~930 cm^{-1} that is not found for the FR10/80 fluoroelastomer. In addition, the position of the absorbance peak between 850 cm^{-1} and 800 cm^{-1} for the FR10/80 (830 cm^{-1}) and FR17/75 (820 cm^{-1}) fluoroelastomers are different.

The presence of a shoulder on the absorbance peaks at 1350 cm^{-1}, and peaks at 930 cm^{-1} and 820 cm^{-1} are characteristic of the FR17/75 fluoroelastomer, whereas a shoulder on the absorbance peak at ~1350 cm^{-1}, a peak at 830 cm^{-1} and no peak at ~930 cm^{-1} are characteristic of an FR10/80 fluoroelastomer.

There are differences in the IR spectra of the LR6316/75 and FR25/80 fluoroelastomers between 950 cm^{-1} and 700 cm^{-1}. The FR25/80 fluoroelastomer has a weak absorbance peak at ~830 cm^{-1} that is not present in the spectrum of the LR6316/75 fluoroelastomer whereas the LR6316/75 fluoroelastomer has absorbance peaks at ~820 cm^{-1} and ~790 cm^{-1} that are not present in the FR25/80 fluoroelastomer spectrum.

The position of the major absorption peak between 950 cm^{-1} and 700 cm^{-1} also varies. The major peak is at ~888 cm^{-1} for the
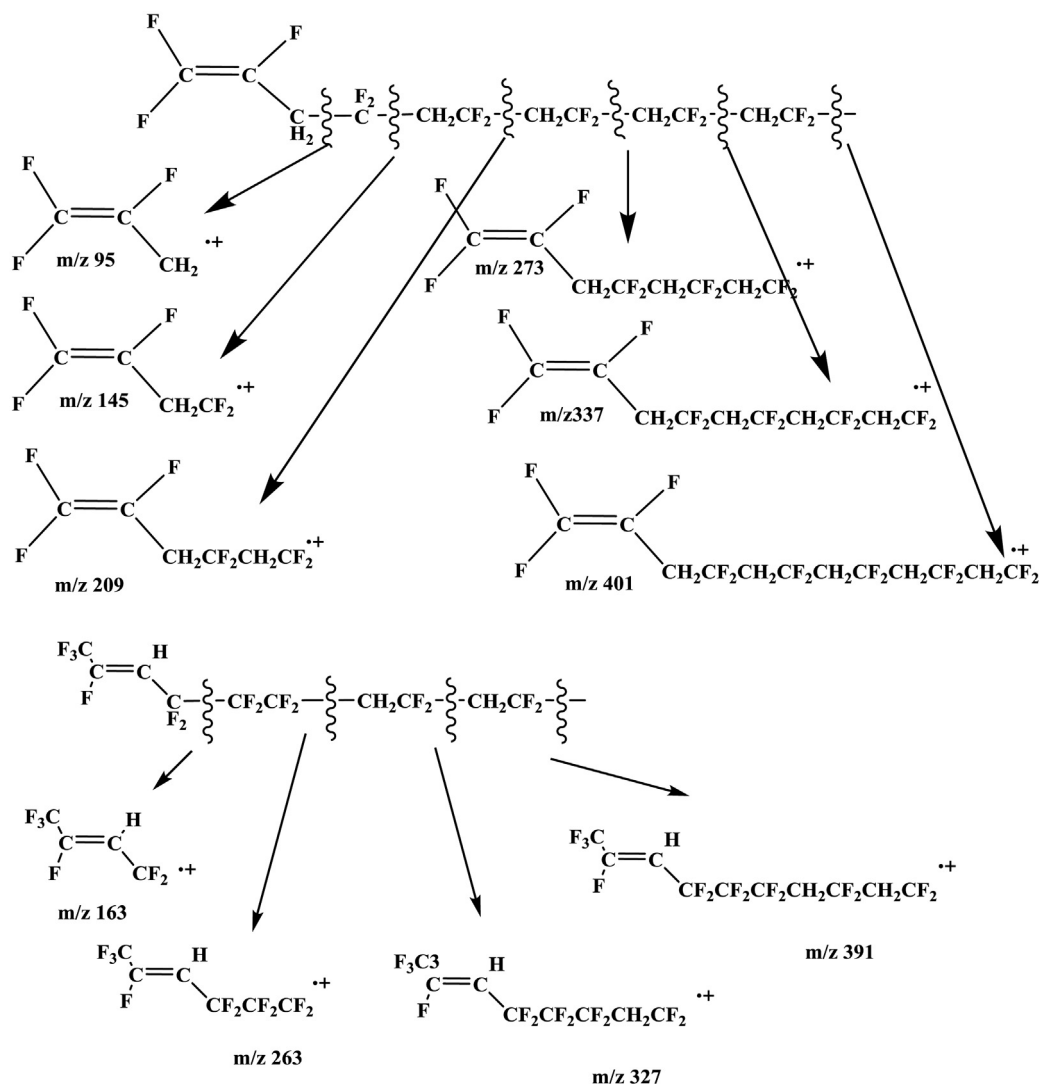
Fig. 13. Potential pathways for the formation of some of the ions in the mass spectra of the major degradation products of FR17/75.

FR17/75 and LR6316/75 fluoroelastomers and at ~880 cm^{-1} for the FR10/80 and FR25/80 fluoroelastomers.

3.4. Pyrolysis gas chromatography/mass spectrometry

Pyrograms of the FR10/80 fluoroelastomer following pyrolysis at 900 °C, 800 °C, and 700 °C are shown in Fig. 7 (retention times between 0 and 40 min) and Fig. 8 (retention times between 3.5 and 15.0 min). Pyrolysis was carried out at three temperatures to determine if a change in the pyrolysis temperature would affect either the number or abundance of the degradation products. Comparison of the pyrograms for a particular elastomer indicated that the thermal degradation products were little affected by the pyrolysis temperature. On the basis of this, it was decided to use a pyrolysis temperature of 700 °C for all subsequent analysis.

The pyrograms of the four fluoroelastomers are shown in Fig. 9. The fingerprint of each of the fluoroelastomers is different. Each elastomer yields degradation products and degradation product intensities that differ from those of the other three elastomers. Some of the peaks, and therefore the compounds that give rise to them, are found in more than one elastomer. The FR10/80 fluoroelastomer has major peaks at 8.72, 10.97, 11.66, and 14.10 min. The peaks at 8.72 and 14.10 min are the most intense. The FR17/75 fluoroelastomer has major peaks at 5.73, 6.76, 6.90, and 8.73 min. The

peaks at 6.76 and 8.73 min are the most intense. The LR6316/75 fluoroelastomer has major peaks at 6.93, 7.36, 7.97, and 8.74 min. The peaks at 6.93 and 7.36 min are the most intense. The FR25/80 fluoroelastomer has major peaks at 8.73, 9.09, 11.02, and 14.27 min. The peak at 9.09 and 8.73 min are the most intense.

The mass spectra of the compounds giving rise to the most intense peaks in the pyrograms of the FR10/80 fluoroelastomer are shown in Fig. 10. The major ions in the mass spectra of the four degradation products of the FR10/80 fluoroelastomer are similar. Potential pathways to the formation of some of the ions in the mass spectra of the major degradation products of the FR10/80 fluoroelastomer are shown in Fig. 11.

The ion with m/z 163 is the most intense in all four mass spectra. This corresponds to an ion with a molecular formula $(C_4F_6H)^{\bullet+}$. Lonfei et al. [11] indicate that this ion $(CF_2CHCF(CF_3)^{\bullet+})$ is produced from the degradation of fluoropolymers with $(-CF_2CH_2CF(CF_3)-)$ sequences along the polymer backbone. This sequence is characteristic of fluoroelastomers composed of vinylidene fluoride and hexafluoropropylene. The ions with m/z 133 and m/z 113 correspond to ions with molecular formulas $(C_3F_5H_2)^{\bullet+}$ and $(C_3F_4H)^{\bullet+}$ respectively.

Analysis of the ions resulting from the degradation products of FR10/80 indicate they are also consistent with those arising from
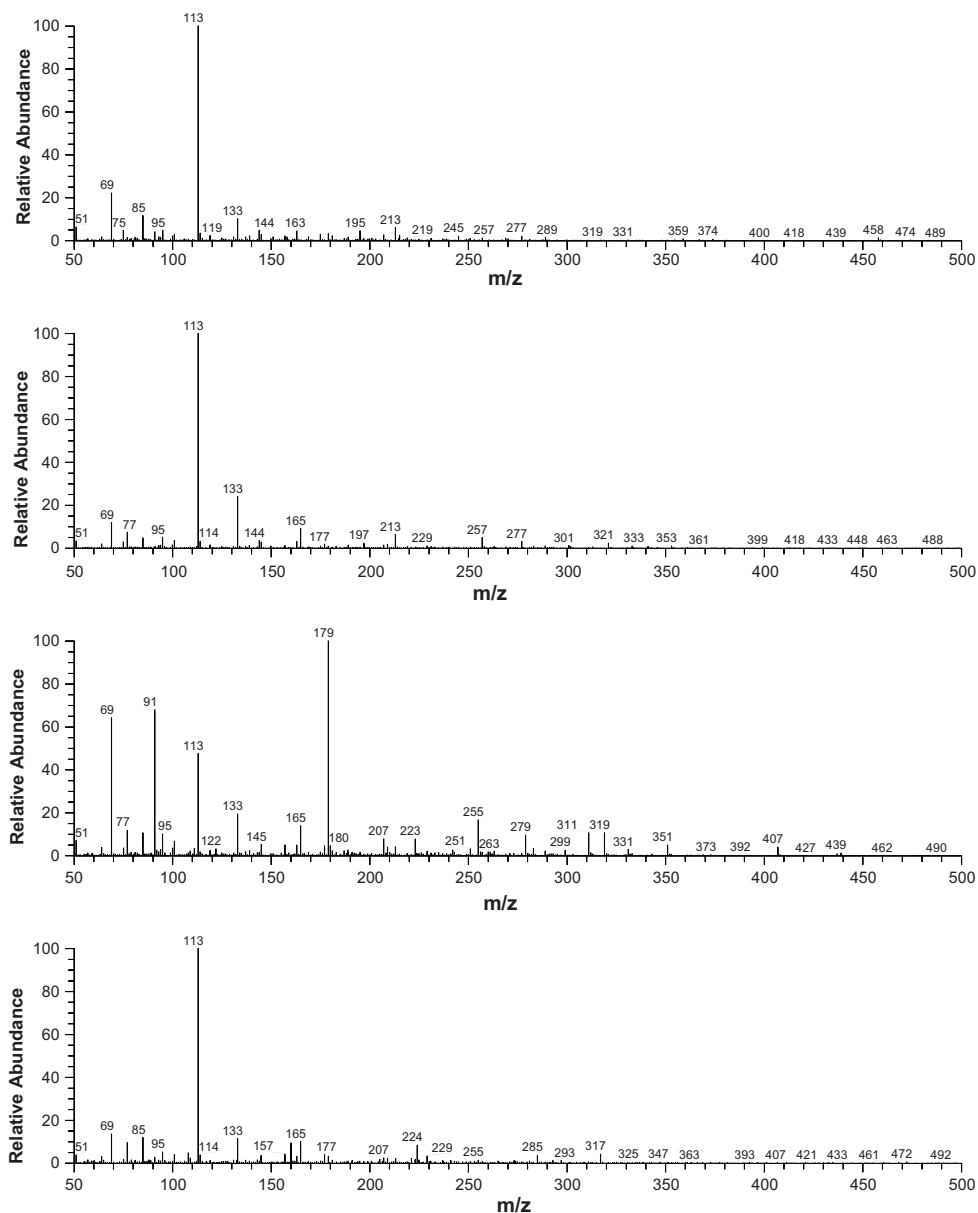
Fig. 14. Mass spectra, from top to bottom, of peaks at 4.03 min, 6.92 min, 7.36 min, and 8.74 min in the pyrogram of the LR6316/75 fluoroelastomer.

a polymer composed of vinylidene fluoride and hexafluoropropylene. For the degradation product at 8.73 min, the mass spectrum has ions separated by 20 mass units at m/z 407 and 387, m/z 387 and 367, and m/z 133 and 113. These are consistent with fragment ions that differ only in the loss of HF from the higher mass ion in the pairs. The mass spectrum also has several ions separated by 50 mass units (m/z 387 and 337 and m/z 367 and 317) that are consistent with fragment ions that differ only in the loss of CF_2 from the higher mass ion. There are also a number of ions separated by 64 mass units (m/z 399 and 335, m/z 337 and 273, m/z 335 and 271, m/z 291 and 227, m/z 271 and 207, m/z 227 and 163) that are consistent with fragment ions that differ only in loss of $C_2H_2F_2$ (vinylidene fluoride) from the higher mass ions.

The major ions in the mass spectra of the four major degradation products of the FR17/75 fluoroelastomer shown in Fig. 12 vary. Ions at m/z 163, 113, and 133 are the most intense for the degradation products at 6.76 min and 8.43 min. However, the mass spectrum of the degradation product at 6.90 min has an ion at m/z 165 that is more intense than the ion at m/z 163 and the degradation product

at 5.72 min has its major at m/z 209. Differences in the degradations products produced by the FR17/75 fluoroelastomer compared to the FR10/80 fluoroelastomer result from the difference in composition of the two elastomers. The FR10/80 fluoroelastomer is a copolymer of VF_2 and HFP while the FR17/75 fluoroelastomer is a terpolymer of VF_2, HFP and TFE.

Potential pathways to the formation of some of the ions in the mass spectra of the major degradation products of the FR17/75 fluoroelastomer are shown in Fig. 13. As was observed for the mass spectra of the degradation products of the FR10/80 fluoroelastomer, the mass spectra of the FR17/75 fluoroelastomer degradation products have ions that are unique to them. Many of the ions in the mass spectra of each of the degradation products differ in mass by 20, 50, 64, and 100 units. These are consistent with ions whose structures differ only in the loss of HF (20), CF_2 (50), $C_2H_2F_2$ (64), or C_2F_4 (100). The major difference in the mass spectra of FR17/75 and FR10/80 are the presence of ions that differ in mass by 100 units. These result from the degradation of portions of the elastomer containing tetrafluoroethylene.
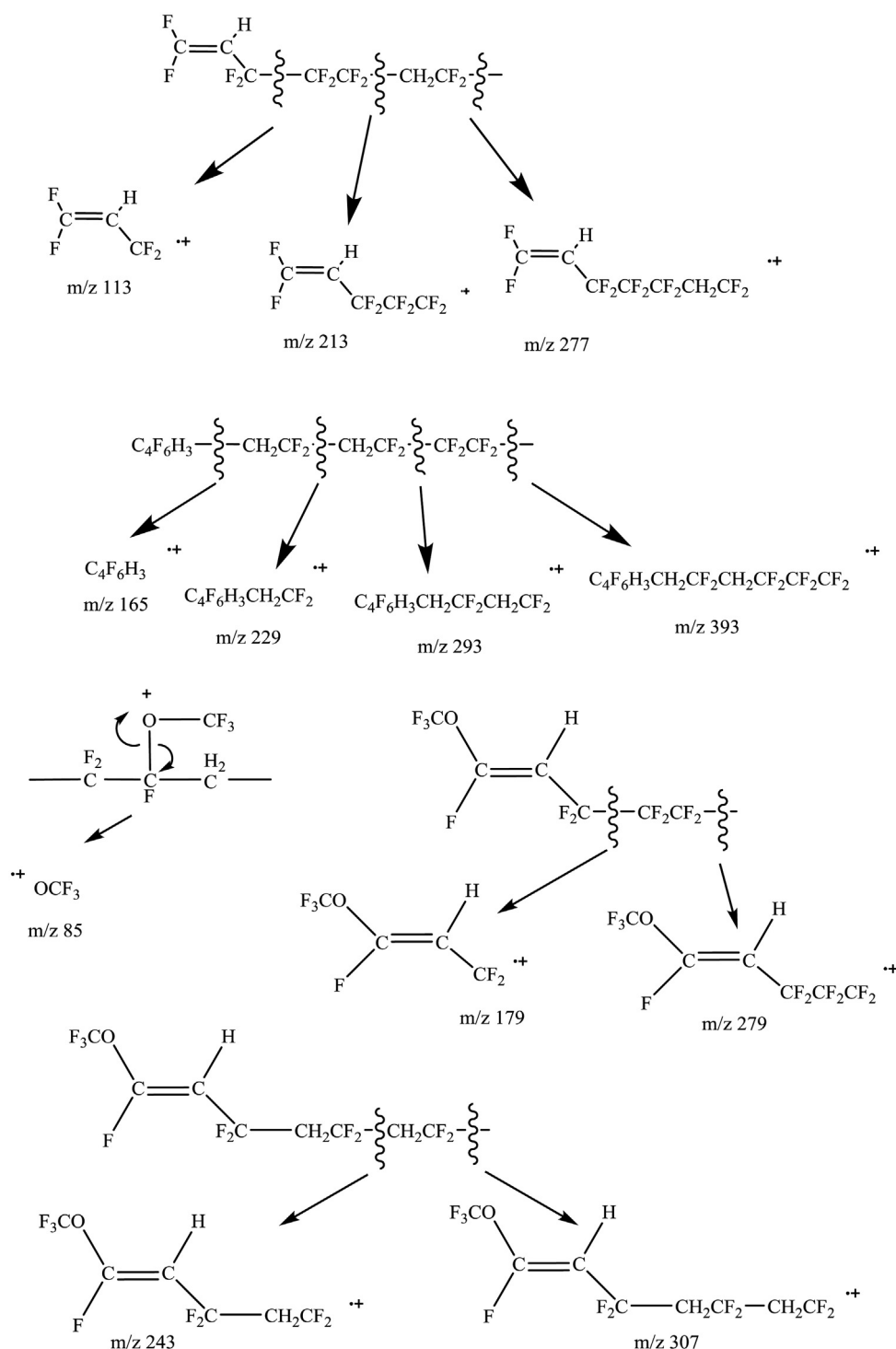
Fig. 15. Potential pathways for the formation of some of the ions in the mass spectra of the major degradation products of the LR6316/75 and FR25/80 fluoroelastomers.

The mass spectra of the four major degradation products of the LR6316/75 fluoroelastomer are shown in Fig. 14. This elastomer has perfluoro(methyl vinyl ether) incorporated to improve its low temperature properties but does not contain hexafluoropropylene. Potential pathways for the formation of some of the ions seen in the mass spectra of the major degradation products of LR6316/75 are shown in Fig. 15.

One ion that would be expected to be found in compounds containing perfluoro(methyl vinyl ether) has a m/z of 85. This ion is formed by the cleavage of the C—O bond of the ether linkage. An ion

with a m/z of 85 is found in the mass spectra of all four degradation products. The major ion in mass spectrum of the compound with a retention time of 7.36 min has a mass 179. Lonfei et al. [11] observed this ion in the mass spectra of fluoropolymers containing perfluoro(methyl vinyl ether). This ion ($CF_2CHCF(OCF_3)^{\bullet+}$) is produced from the degradation of fluoropolymers with ($-CF_2CH_2CF(OCF_3)-$) sequences along the polymer backbone. This compound also has an ion at m/z 279 which is indicative of a $-CF_2CF_2-$ sequence adjacent to the structure that gave rise to the ion with mass 179.
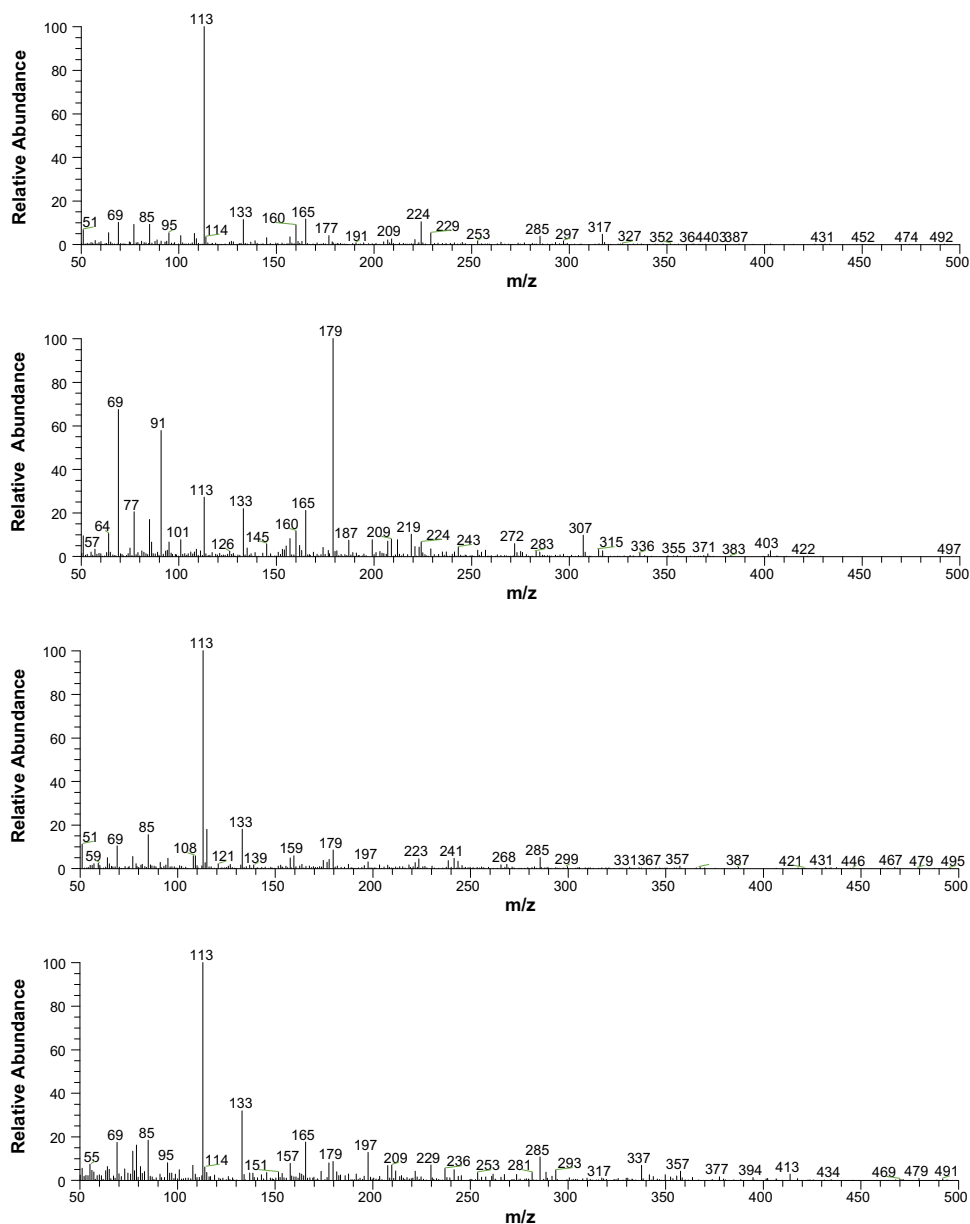
Fig. 16. Mass spectra of peaks (from top to bottom) at 8.73 min, 9.09 min, 11.02 min and 14.27 min in the pyrogram of the FR25/80 fluoroelastomer.

As was observed for the FR10/80 and FR17/75 fluoroelastomers, many of the ions in the mass spectra differ in mass by 20, 50, 64, and 100 units. These are characteristic of ions that differ only in the loss of HF, CF_2, $C_2F_2H_2$, and C_2F_4 from the higher mass ion respectively.

The mass spectra of the major degradation products of the FR25/80 fluoroelastomer are shown in Fig. 16. FR25/80 contains the same monomers as were used to prepare the LR6316/75 fluoroelastomer, although the relative amounts of the monomers differ from one elastomer to the other. For the major degradation products for the LR6316/75 fluoroelastomer all the mass spectra have an ion with m/z 85 that arises from the cleavage of the C—O ether bond of the perfluoro(methyl vinyl ether) component of the elastomer. The major ion in the mass spectrum of the compound a retention time of 9.09 min has a mass of 179. As was indicated for the LR6316/75 fluoroelastomer, this ion is indicative of a fluoropolymer with ($-CF_2CH_2CF(OCF_3)-$) sequences along the polymer backbone. However, this compound also has ions at mass 243 and 307 that are indicative of one and two $-CH_2CF_2-$ sequences respectively adjacent to the structure that gave rise to the ion with mass 179.

In addition, there are ions in the mass spectra that differ in mass by 20, 50, 64 and 100 mass units. These arise from fragmentation of the degradation products in ways similar to those described for the other three elastomers.

4. Conclusions

The py-GC/MS identification of four commercial fluoroelastomers has been described. Each of the elastomers has a unique pyrogram that can be used to identify it. In addition, the mass spectra of the major degradation products of the four elastomers can be related to the monomeric compounds used in their preparation; that is, they are consistent with the degradation of fluoroelastomers synthesized from vinylidene fluoride and hexafluoropropylene, vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, or vinylidenefluoride, tetrafluoroethylene and perfluoro(methyl vinyl ether).

Although FT-IR can also be used to identify unadulterated samples of the fluoroelastomers studied in this paper, fluoroelastomers

that have been in service could be contaminated. For instance, the presence of oil or other chemicals in a sample could mask some of the IR peaks used to identify an elastomer. The py-GC/MS identification of fluoroelastomers that have been in service is not affected by adulterants. The degradation products of adulterants are separated and can be identified or differentiated from those arising from the fluoroelastomer.

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